KEY ENVIRONMENTAL CLEANUP CONSIDERATIONS FOR ETHANOL AND ALKYLATES

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OBJECTIVES

- REVIEW THE REMEDIATION AND TREATMENT OF ETHANOL
- REVIEW THE REMEDIATION AND TREATMENT OF ALKYLATES
- CONSIDER IMPACTS OF INCREASED USE OF ETHANOL AND ALKYLATES ON SUBSURFACE CLEANUPS

ETHANOL CHARACTERISTICS

- INFINITELY SOLUBLE IN WATER (far more than benzene or MTBE)
- VERY LOW HENRY'S CONSTANT (far less volatile from water than benzene or MTBE)

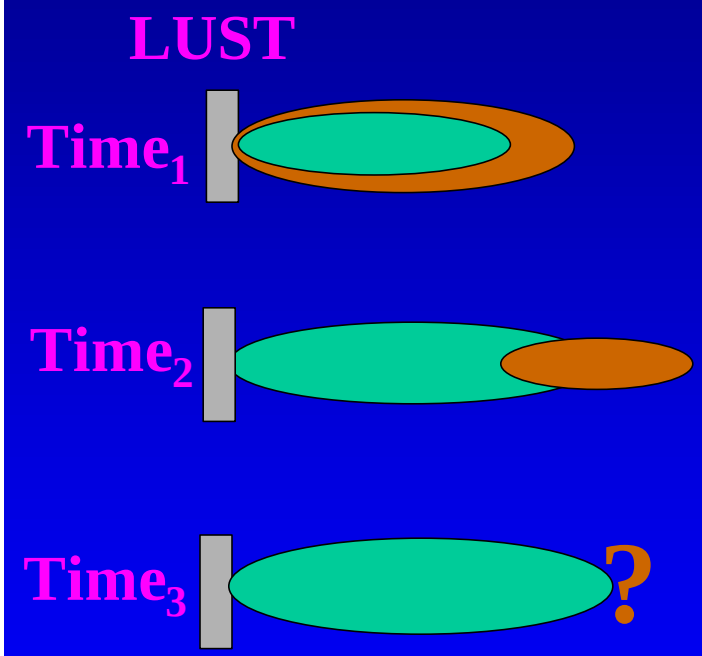
✍ OVER TIME, ETHANOL WILL PRIMARILY OCCUR IN THE DISSOLVED PHASE, AND NOT IN THE NAPL OR VAPOR PHASES

ETHANOL CHARACTERISTICS

- ETHANOL ADSORPTION TO ORGANIC MATTER IS QUITE MINIMAL (far less than benzene, less than MTBE)
- HIGHLY BIODEGRADABLE, BOTH AEROBICALLY AND ANAEROBICALLY (more than benzene, much more than MTBE)

✍ETHANOL PREFERS DISSOLVED PHASE, BUT MAY BIODEGRADE QUICKLY IN SUBSURFACE

BTEX & ETHANOL PLUMES



BTEX & Ethanol plumes growing

BTEX plume now stable;
Ethanol readily degrading

Ethanol plume gone???

Based on modeling by Molson et al., 2000

ETHANOL BIODEGRADATION

- VARIOUS LABORATORY STUDIES SUGGEST AEROBIC HALF LIFE OF ETHANOL IN SOIL & GROUNDWATER OF 0.1 TO 5 DAYS => RAPID BIODEGRADATION (2-8 times faster than BTEX)
- BUT ARE LAB RATES REPRESENTATIVE OF FIELD CONDITIONS???
- FIELD VERIFICATION OF ETHANOL BIODEGRADATION RATES IS SEVERELY LACKING…

ETHANOL BIODEGRADATION IMPACTS ON BTEX PLUMES

- ETHANOL PREFFERRENTIALLY DEGRADED. RAPID AEROBIC BIODEGRADATION OF ETHANOL MAY UTILIZE MOST DISSOLVED OXYGEN (and/or nutrients)
- AEROBIC BTEX BIODEGRADATION SLOWED AND/OR DELAYED BY PRESENCE OF ETHANOL (various studies)
- BTEX PLUME LENGTHS MAY INCREASE BY:
  - 16-34% (Malcolm Pirnie, 1998)
  - 25% (Governor's Ethanol Coalition, 1999)
  - 20-100% (LLNL, 1999)
  - 20-100%, or more (Molson et al., 2000)

CO-SOLVENCY DUE TO ETHANOL'S PRESENCE

- LAB EXPERIMENTS SUGGEST THAT 10% ETHANOL (10,000 PPM in water) MAY INCREASE BTX LEVELS IN WATER 33%
- ETHANOL LEVELS OF 10,000 PPM ARE UNLIKELY TO EXIST FOR LONG AT ETHANOL-ENRICHED GASOLINE SPILL SITES
- ETHANOL LEVELS DO EXCEED 10,000 PPM AT NEAT ETHANOL SPILLS (data from 3 sites)
- THUS AT TERMINALS, STARTING BTEX LEVELS MAY BE ELEVATED, AND BTEX BIODEGRADATION RATES SLOWED - A NEGATIVE SYNERGISTIC EFFECT?

ENHANCED GASOLINE MOBILITY DUE TO ETHANOL'S PRESENCE

- NEAT ETHANOL IS USED AS SURFACTANT IN OIL E&P ACTIVITIES, TO INCREASE MOBILIZATION OF OIL FROM THE MATRIX
- ETHANOL LEVELS FROM SPILLS OF ETHANOL-ENRICHED GASOLINE LIKELY TOO LOW TO CREATE THIS EFFECT
- BUT, NEAT ETHANOL SPILLS AT BLENDING TERMINALS CAN CREATE THIS EFFECT ON PETROLEUM-IMPACTED SOILS

✍ THUS "IMMOBILIZED" RESIDUAL PRODUCT CAN BECOME MOBILIZED…

Maximum Measured Field Concentrations of Ethanol From Different Release Scenarios

Release Scenario	Max. Measured Ethanol Conc. (mg/L)
Spill of neat/denatured ethanol (97 - 100% EtOH)	81,000
Spill of ethanol-blended gas (24% EtOH – in Brazil)	2,503
Spill of ethanol-blended gas (10% EtOH)	0.65
Coated bentonite pellets	1,200

Field data are very limited; < 12 sites nationwide in USA

ETHANOL FATE & TRANSPORT SUMMARY

- ETHANOL ITSELF SHOULD READILY BIODEGRADE
- MAY DELAY BTEX BODEGRADATION AT GASOLINE SPILLS, THUS INCREASING BTEX PLUME LENGTHS
- AT NEAT ETHANOL SPILLS (terminals), CO-SOLVENCY MAY INCREASE BTEX LEVELS AND RESIDUAL GASOLINE NAPL MAY BECOME MOBILIZED
- VERY LITTLE FIELD DATA EXISTS

ETHANOL REMEDIATION

- CHARACTERISTICS THAT HURT:
  - High Solubility
  - Poor Adsorption To Carbon
  - Poor Volatility (low Henry's Constant)
- CHARACTERISTICS THAT HELP:
  - Very biodegradable

ETHANOL REMEDIATION

TECHNOLOGY	APPLICABILITY
GROUND-WATER EXTRACTION	As usual, good for plume control; fair for site remediation
SOIL VAPOR EXTRACTION	Ethanol's low volatility makes extraction portion ineffective; added oxygen may be quite beneficial
AIR SPARGING	Ethanol's low "stripability" makes aeration questionable, though added oxygen may be quite beneficial
ENHANCED BIODEGRADATION	Expected to be excellent; natural biodegradation rates may be so fast that enhancement rarely needed

ETHANOL REMEDIATION
MONITORED NATURAL ATTENUATION

- ETHANOL ITSELF EXPECTED TO NATURALY ATTENUATE QUITE WELL
- ETHANOL'S PRESENCE MAY NEGATIVELY IMPACT MNA OF OTHER GASOLINE COMPOUNDS AS:
  - BTEX PLUMES LONGER LIVED, AND GREATER LENGTH (16-100% longer? more?)
  - BTEX/TPH ELEVATED WHEN NEAT ETHANOL SPILLED (co-solvency)
  - FREE PRODUCT MORE MOBILE

TREATMENT OF ETHANOL-IMPACTED WATER

TECHNOLOGY	APPLICABILITY
AIR STRIPPING	Ethanol's very high solubility and very low Henry's Constant means air stripping quite ineffective
CARBON ADSORPTION	Ethanol's poor adsorption to organic matter makes use of GAC likely to be quite poor
ADVANCED OXIDATION	Expected to be effective as ethanol readily oxidized; little data available
BIOTREATMENT	Expected to be excellent under a wide-variety of conditions

REMEDIATION IMPACTS OF USING MORE ETHANOL

- HARDLY ANY FIELD KNOWLEDGE EXISTS (or even ground-water concentration data!)
- UNSETTLING…NEED MORE FIELD INFORMATION!!!
- ETHANOL BIODEGRADES SO READILY THAT ETHANOL PLUMES THEMSELVES PROBABLY NOT A PROBLEM AT GASOLINE RELEASE SITES (needs verification)

REMEDIATION IMPACTS OF USING MORE ETHANOL

- ENLARGED BTEX PLUME COULD BE PROBLEMATIC AT SOME GAS SPILL SITES
- ENLARGED BTEX PLUME AND/OR REMOBILIZATION OF RESIDUAL NAPL LIKELY TO BE PROBLEM AT TERMINALS
- HIGH TASTE THRESHOLDS FOR ETHANOL COULD ALLOW FOR LONGER-TERM CONSUMPTION OF ETHANOL-IMPACTED DRINKING WATER (and possibly BTEX)

ALKYLATES CHARACTERISTICS

- BROAD SUITE OF C_6 – C_9 BRANCHED ALKANE COMPOUNDS
- COMPRISE ROUGHLY 14% OF GASOLINE (varies)
- HIGH OCTANE (92-94)

ALKYLATES CHARACTERISTICS

- LOW SOLUBILITY IN WATER (less than BTEX, far less than ethanol)
- ADSORB WELL TO SOIL ORGANIC MATTER (more retarded than BTEX, far more than ethanol)
- HIGH HENRY'S CONSTANT (more volatile from water than benzene, far more than ethanol)
- MODERATE BIODEGRADABILITY (less than BTEX, far less than ethanol)

ALKYLATES REMEDIATION

- USED IN GASOLINE FOR DECADES, THUS WE HAVE DONE LOTS OF ACTIVE REMEDIATION AND MNA PROJECTS ON ALKYLTAES (but, not much alkylate-specific data available)
- STANDARD GASOLINE REMEDIATION & TREATMENT METHODS HAVE WORKED ON ALYLATES IN THE PAST
- THEY SHOULD CONTINUE TO DO SO IN THE FUTURE

ALKYLATES REMEDIATION

- WITH HIGH RETARDATION & SLOW LEACHING, WILL INCREASED ALKYLATES USAGE MEAN EVEN MORE HYDROCARBON MASS TIED UP IN SOIL LONGER?
- DOES THIS MAKE RBCA OUTCOMES BETTER? WORSE?
- DOES THIS MAKE MNA BETTER? WORSE?

IN-SITU REMEDIATION

	BTEX	ALKYLATES	ETHANOL
MNA	Great	Good - great?	Great, but BTEX MNA worse?
PRODUCT RECOVERY	Good	Good?	Fair-good?
PUMP & TREAT	Good	Good?	Good?
AIR SPARGE	Good	Good – great?	Good?
SVE	Great	Good – great?	Good?
ENHANCED BIO.	Good	Good – great?	Great (if needed)

WATER TREATMENT

	BTEX	ALKYLATES	ETHANOL
AIR STRIPPING	Great	Good?	Poor?
GRANULATED ACTIVATED CARBON	Great	Good – great?	Poor?
BIOTREATMENT	Good	Good- great?	Great
ADVANCED OXIDATION PROCESS	Good	Good?	Good?

ETHANOL CONCLUSIONS

- FATE, TRANSPORT, REMEDIATION & TREATMENT KNOWLEDGE
  - THEORETICAL KNOWLEDGE = GOOD
  - FIELD BASED KNOWLEDGE = POOR TO NON-EXISTENT
- PHYSICAL & CHEMCIAL REMEDIATION & TREATMENT METHODS LIKELY BAD (air stripping, GAC)
- BIOLOGICAL REMEDIATION & TREATMENT METHODS LIKELY VERY GOOD (MNA, enhanced bioremediation, ex-situ biotreaters)
- BEWARE NEGATIVE IMPACTS ON BTEX PLUMES

Reference: Davidson, J.M., and Creek, D.N., 2000. "The Fate, Transport, and Remediation of the Gasoline Additive Ethanol". In Proceedings, *Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation*, National Ground Water Assoc., Westerville, OH, pp. 265-277.

ALKYLATES CONCLUSIONS

- FATE, TRANSPORT, REMEDIATION & TREATMENT KNOWLEDGE
  - THEORETICAL KNOWLEDGE = FAIR
  - FIELD BASED KNOWLEDGE = FAIR

  BUT NOT MUCH AYLKLATE-SPECIFIC INFO!
- PHYSICAL & CHEMICAL REMEDIATION & TREATMENT METHODS LIKELY GOOD
- BIOLOGICAL REMEDIATION & TREATMENT METHODS LIKELY GOOD (MNA, enhanced bioremediation, ex-situ biotreaters)
- LACK DIRECT DATA ON ALKYLATES (revise sampling & analyses approaches?)

UNCLEAR ISSUES

- WOULD CO-OCCURRENCE OF ETHANOL AND ALKYLATES HAVE SYNERGISTIC EFFECTS?
  - ETHANOL INCREASE SOLUBILITY & MOBILITY OF ALKYLATES?
  - WILL THEY LIMIT/DELAY ONE ANOTHER'S BIODEGRADATION?
  - LIMIT/DELAY BTEX BIODEGRADATION?
  - MANDATE ACTIVE REMEDIATION AND TREATMENT OF GASOLINE RELEASES MORE OFTEN THAN AT PRESENT?